

# SCIENCE FOR CERAMICS PRODUCTION

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## PARTICULARITIES OF THE TECHNOLOGY FOR PRODUCING HIGH-DENSITY TECHNICAL CERAMICS. ACTIVITY OF OXIDE POWDERS DURING SINTERING<sup>1</sup>

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Possible ways to increase the energy of oxide powders during calcination and ways to activate them are examined. This is accomplished in the following cases: first, increasing temperature, i.e., input of heat energy; second, increasing internal energy by means of surface energy and surface defects during mechanical grinding; third, increasing internal energy by chemical methods of production under strongly nonequilibrium conditions as a result of the surface energy and defects on the surface and in the bulk; and, fourth, increasing the internal energy with the introduction of additives via the energy of lattice deformation occurring with the introduction of foreign ions in general, since no two ions are of the same size, and the energy of lattice defects with the introduction of heterovalent ions.

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In the fabrication of ceramic articles, sintering is the principal concluding stage of the entire technological cycle at which their user properties are formed. We note that ceramics are, usually, articles and materials made of a mineral initial material obtained by sintering powder blanks [1].

The purpose of the present article is to examine ways to intensify the calcination of oxide powders in order to obtain technical ceramic with prescribed functional characteristics.

It is known [2] that because of mass transfer densification and hardening of a powder body occur under conditions of thermal activation as a result of the dissipation of the excess energy of the powder (as compared with the energy of the monolith). The driving force of the process is the surface tension of the dispersed particles, which is what causes them to coalesce, just as drops of liquid or glass coalesce. However, the physical mechanisms of mass transfer under these conditions are different: atom-wise motion of matter — diffusion — occurs in the first case and a viscous cooperative flow of atoms occurs in the second case. Therefore, a neces-

sary condition for obtaining a ceramic is that the initial body must reach a state where the energy of its constituent particles is higher than for a monolith.

On this basis, in [3] it is proposed that the technological process of obtaining a ceramic be viewed in general as three basic changes which occur in one way or another. These changes are obtaining the powder (if the initial material no longer consists of finely dispersed particles, for example clay, kaolin, and so forth) and the formation and calcination of the intermediate product, during which sintering occurs.

It should be noted that separate problems are solved at each of the steps. The goal at the first step is for the powder particles to accumulate energy. This step establishes the driving force for sintering. At the second step blanks with the required shape and dimensions are obtained — i.e., here the quality of the finished article is determined with respect to these parameters. The structure of the final product, which determines its user's properties — physical, chemical, aesthetic, ecological, sanitary, and so forth — is formed at the third step. The blank at this stage consumes the energy stored in the accumulating structures — energy of the free surface and its defects as well as the energy the defects in the volume of the particles — for densification and hardening. Energy is dissipated during mass transfer against the background of thermal activation [2].

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<sup>1</sup> We are continuing the publication of articles united by a common theme (see the 2008 issues Nos. 2 – 4 and 6 – 8).

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The special feature of ceramics, just as other solids, i.e., the main factor distinguishing them from liquids and gases, is the long time constant in all interaction processes. This is due to their high viscosity even at premelting temperatures. Thus, refractories at the softening onset temperatures (1300 – 1700°C) possess viscosity of about  $10^8 \text{ Pa} \cdot \text{sec}$  depending on the chemical composition. Consequently, at ordinary temperatures there is not enough time for them to dissipate the energy delivered to them in fast, energy-saturated, nonequilibrium, irreversible processes, and they accumulate energy.

The accumulated excess energy can be dissipated with a decrease of viscosity of the object, i.e., when the mobility of its constituent elements increases, for example, during thermal activation. Increasing the temperature, we increase the energy of the body. The Clausius – Clapeyron equation for the state of a mole of matter indicates this possibility:

$$pV = RT,$$

where  $p$  is the pressure,  $V$  is the volume,  $T$  is the temperature, and  $R$  is a constant, J/K.

According to the existing ideas [4], the physical mechanism of the process is the formation of equilibrium vacancies by means of energy fluctuations. Another form of activation, i.e., a change of the product  $pV$  during the process, is technically difficult to accomplish. Consequently, in practice, solids are worked during heating under isobaric conditions, under which a thermal change of volume is observed in the case where there is an energy imbalance.

Oxygen compounds (oxides), which are constituents of a ceramic, possess strong and directional ion-covalent chemical bonds. As a result the mobility of the atoms (ions) decreases considerably, i.e., the viscosity of such objects increases compared with metals and alloys. In addition, unit cells of considerable size are formed from two or more types of atoms, which in general have different radii, sign and magnitude of the charge, and chemical nature [5]. As a rule, they contain several formula units and consist of two or more sublattices.

As a result of such a structure, extended defects of crystals (dislocations, boundaries, and so forth) and their slip surfaces have a complicated topology, which practically stops their cooperative motion [6]. All this intensifies the inertness, the resistance to external chemical, mechanical, and other actions, generally inherent to a solid body and in the case of ceramics right up to pre-melting temperatures. Glass-like (amorphous) phases with similar compositions also possess high viscosity and are inert with respect to external actions.

All this elucidates the reasons why coarse-grain ceramic powders do not sinter even when heated up to pre-melting temperatures — only 100 – 200°C below the melting point.

Ceramic technology began with the use of clays and kaolins, i.e., sedimentary rocks, where the sizes of the constituent particles are practically in the nanometer range, as the

initial materials. However, they did not meet certain special requirements, and the list of such materials expanded rapidly. Therefore, for non-clay coarse-grain initial material it was necessary to find other ways to activate sintering other than thermal only.

In the course of the investigations performed in different countries it was determined that activation of sintering, i.e., increasing its rate and decreasing its temperature and duration, can be accomplished by using powders ground to particle sizes of the order of a micron. In this case, the inertness of a solid makes it impossible for the energy accumulated by the particles during the creation of new surfaces in the course of grinding to be dissipated. The energy is retained right up to high temperatures, and it is dissipated by means of mass transfer via diffusion over quite considerable distances. Diffusion fluxes determine the sintering processes in which the body lowers the stores of surface energy.

Ordinarily, powders are dispersed by grinding with milling bodies in various types of mills. The main objective of the grinding is to obtain particles with the required sizes and size distribution by external mechanical action. There are two possible mechanisms for energy to accumulate in the particles: the movement of ions and rearrangement of their chemical bonds during elastic and plastic deformation and the creation of new surfaces by the destruction of particles. We note that in the case of ceramics plastic deformation is observed only in microvolumes, practically at the point where the particles touch the milling body, since it is only here that a sufficiently high temperature is produced. The re-arrangement of the chemical bonds and the plastic deformation occur at short distances within one unit cell or neighboring unit cells, so that the stresses associated with them are removed even with weak thermal activation. The voids (pores) between the particles are healed only with the movement of ions over appreciable distances, exceeding interatomic distances, by diffusion. As a result of the excess surface energy, densification and hardening of the body, i.e. sintering, are observed precisely in such processes.

The existing data show that milling can give powders with particles of the order of a micron in size [7]. Further milling is ordinarily stopped primarily for two reasons. In the first place, according to the Le Chatelier rule a body strives to lower its energy by reverse processes of conglomeration, sticking of particles under the action of adhesive forces. In the second place, the increasingly more dispersed powders obtained by milling practically do not break down because of the high strength of small single-crystalline particles.

We call attention to a basic feature of powders obtained by mechanical dispersal — the particles retain the crystal structure, although it is possible to achieve high degrees of lattice distortion, right up to the formation of amorphized surface layers. They are metastable and far from a state of equilibrium because of the extended nature of the free surface and because of the presence of excess lattice defects — vacancies, dislocations, stacking faults, and so forth mainly in surface layers. In other words, they possess a high surface

energy and energy of defects of the surface and near-surface layers.

Thus, in the present case we can probably talk about one or another form of activation of a solid together with thermal activation, specifically, mechanical activation [8]. It is expressed as the formation of new interfaces (with their energy) and the appearance of defects and mechanical stresses associated with them (with their energy). It should be noted that actually these two processes increase the product  $pV$  in the equation of state indicated above. But this accumulated energy is spent in dissipation processes.

Some authors believe that it is the defects that are responsible for the activity, but practice shows that the stresses associated with defects relax already at low temperatures and have no effect on sintering [9].

Another way to obtain highly dispersed powders are chemical methods, based on, specifically, crystallization from solutions (precipitation) and destruction of salts, cryogenic or plasma processes, and so forth [10]. Their main feature is that the conditions under which they occur lie in regions far from equilibrium and, as a rule, they are non-stationary. As a result, the growth of embryos of a solid phase actually stops at the stage of nucleation of crystals — very defective particles, possessing highly extended outer and inner surfaces. As a rule, they have a round shape and a strongly distorted crystalline structure [11, 12].

Practice shows that highly dispersed oxide powders obtained by means of modern chemical technologies possess high activity during sintering. For example, the temperature of the process decreases by 200 – 300°C with the density exceeding 98 – 99% of the theoretical value [13]. Ordinarily, the dispersity of these powders is characterized by “less than a micron,” i.e., it lies in the nanometer range. As a rule, powders consist of comparatively large aggregates (5 – 10  $\mu\text{m}$  or larger), which themselves consist of small particles of the order of tens of nanometers in size, which are bound to one another by adhesion forces.

When a solid particle arises under strongly nonequilibrium conditions, the overlapping of the chemical bonds of neighboring atoms is quite disordered and random with a large number of different kinds of structural imperfections arising. Such processes result in the appearance of materials with a loose structure, and the surfaces are fractal, i.e., very extended [14]. The surface of such particles has a high degree of “natural roughness,” i.e., besides sites where crystal boundaries and dislocations emerge, it contains a large number of depressions, ledges, angles, single adsorbed atoms, and vacant sites as well as planar defects.

On the basis of general considerations [2], the distribution of defects over the section of a particle is nonuniform and their concentration is higher at the surface. The volume state of the ions is observed only at depths above ten interplanar distances. Consequently, as the powder dispersity increases, the role of near-surface layers in the processes increases, since their fraction in the total volume increases. For

example, corundum particles (i.e.,  $\alpha\text{-Al}_2\text{O}_3$ , crystal lattice parameter  $c \approx 1.3 \text{ nm}$ ) with a BET specific surface area 100  $\text{m}^2/\text{g}$  have a surface-averaged diameter about 15 nm, i.e., ten unit cells fit along it. Therefore, the state of the ions making up such a particle is close to the surface state, so that they possess the corresponding energy, and the particles possess an amorphous structure. Similarly, the surface-averaged diameter of the particles with specific surface area 10  $\text{m}^2/\text{g}$  is 150 nm, and their state, in general, fall between a surface and a volume state.

It should be kept in mind that the surface of highly dispersed particles is qualitatively different from that of large particles, since such powders consist of ions with partially compensated chemical bonds and the cell sites surrounding them are not completely filled. In practice, all such powders are characterized by a metastable state of the particles with elevated free energy. This is manifested in their high sorption capacity for gases and radicals and the capability of following aggregations in time (spontaneous densification) during the production process.

Another aspect of such a state is manifested in the appearance in particles of strong forces due to hydrostatic compression as a result of an increase of the surface tension. Thus, for approximately 1  $\mu\text{m}$  dispersity they equal about 0.5 MPa and increase with decreasing size [15], which can result in “hot self-pressing.” Large compression forces in nanoparticles as well as a high concentration of imperfections are the reasons for their unstable metastable state. On heating, the melting temperature of such powder decreases appreciably as compared with the monolith [2].

It should be underscored that two types of imperfections (defects), responsible for elevated particle energy, are characteristic for nanometer-size particles. Defects of the first type, also characteristic for large objects (obtained by grinding), are displacements of ions from the sites of the regular arrangement (vacancies, dislocations, and so forth) and are related with the presence of local mechanical stresses or surface sections with nonzero curvature. Defects of the second type, characteristic only for the nanometer range, are actually ions with uncompensated chemical bonds as a result of their arrangement on steps, wedges, corners of small particles, slightly greater than the unit cell. It can be said that in these two cases the excess energy is determined by different forces — mechanical stresses or chemical bond — and in general by the chemical bond. The difference is that in the first case we have a deformation and in the second partial compensation of interionic bonds. However, in both cases such energy is characteristic of metastable states of a solid. It is accumulated in irreversible processes, and it is dissipated during mass transfer under thermal activation conditions.

Apparently, in the present case there is one other form of activation — chemical, which depends on an increase of the energy of the powder in the presence of a large number of atoms (ions) with uncompensated bonds. This is determined by their arrangement on steps, ledges, and corners of the

outer fractal surface of the particles. As a result of the small size of the latter and also the large number of structural defects on their surface and in the bulk their state is close to a surface state. Such particles can probably be described using a quasichemical approach [16]. However, it is necessary to take account of the fact that the energy characteristics of surface atoms (ions) are substantially different from the characteristics of atoms (ions) located in the interior volume of crystals [17].

Just as in the preceding case of mechanical activation, here the increase of the energy of the particles is associated with an increase of the product  $pV$  in the equation of state. We note the main differences between the activation mechanisms. In the first case energy accumulates mainly as a result of the generation of stresses accompanying the formation of surfaces with nonzero local curvature as well as the deformation of chemical bonds in near-surface layers. In the second case, the stresses in the particles increase sharply as a result of bond deformation not only on their surface but also in the interior volume as well as because of a sharp increase of the curvature of their surface. In addition, the cofactor  $V$  increases because of the general opening up of the lattice accompanying a transition to the surface state of the particles.

It is noteworthy that the structure and, therefore, the behavior of particles in various processes must differ sharply from the structure and behavior of large particles — micron-size and larger, which follows from other, purely physical considerations. According to a quite rough estimate made by B. B. Kadomtsev [18], the boundary between the microworld, where the quantum theory is applicable, and the macroworld, where classical mechanics is applicable, is determined by the order of magnitude of the particles about 0.1  $\mu\text{m}$ . Correspondingly, these are the minimum sizes of macrobodies and the maximum sizes of microbodies.

Thus, the behavior of nanoparticles can differ substantially from that of larger particles. In the case of real powder bodies one must assume the existence of a certain transitional region which is associated, first and foremost, with the existence of a quite wide particle-size distribution. As the distribution curve shifts, the role of quantum effects associated with the presence of very small particles decreases.

When additives are introduced (so-called modification), in our view, one other form of regulation of the rates of processes in oxide powders is observed. It should be noted that investigations in this direction are only at the beginning stage because of the large number of objects (vapor of the additive — the main component) with their crystal — chemical features. However, investigations performed in the last few years [19] show that the introduction of additives does not change the behavior of the initial powders during sintering; the characteristic features of the densification and hardening processes for coarsely dispersed (greater than one micron) or finely dispersed (less than one micron) particles remain.

Definite advances in obtaining articles with prescribed characteristics can be made with a rational choice of the type

and concentration of the additive. In doing so, one must take account of the fact that only pure initial materials can be used; otherwise, the impurities nullify the action of the additive. Depending on the degree of oxidation of the component introduced (isovalent, heterovalent) this can be a substitution or interstitial solution.

Any additive will deform the matrix lattice (i.e., the force of the chemical bond), since two different ions with the same size do not exist in nature. Definite tensile or compression stresses are associated with this deformation; it is these stresses that give rise to the elevated energy of the particles. In addition, when heterovalent additives are introduced excess defects must form in the ionic and anionic sublattices of the ceramic body must form in order to maintain the overall electric neutrality of the body with ionic-covalent bonds. The excess energy determined by tensile or compressive stresses is also determined by defects. Thus, just as in the two preceding cases of activation, the additives increase the product  $pV$  in the equation of state of the particles. However, this energy is not dissipated during mass transfer, but rather it acts in the entire heat-treatment interval. Depending on the sign of the stresses, it increases or decreases the rate of the processes but the stresses in the lattice remain.

In all cases examined above, for sintering oxide powders thermal activation is necessary in order to decrease the viscosity of the material and thereby conduct the process in a time frame convenient in practice. In all cases examined, the driving force for densification and hardening is the striving of particles to decrease their surface energy and the energy of surface and volume defects. Mechanical activation of powders yields comparatively large crystalline particles with a large size variance. They sinter by means of classical mechanisms of vacancy diffusion from concave to convex sections of the surface [2]. Consequently, as rule, they give ceramics with an unequal grain structure and with comparatively low property indicators with residual porosity up to 3 – 5%.

Under chemical activation, because of the amorphous structure of the highly disperse particles of practically constant size, the driving forces of sintering are sharply increased (sometimes the process is called “hot self-pressing”). Small particles and the small pores between them comprise a viscoplastic medium, which deforms as a whole. The pores are removed along boundaries, which are likewise small in size. The small pores and small boundaries impede the growth of particles, which subsequently increase in size by means of adjustment of small-angle boundaries. The experimental data show that sintering of such powders gives materials with practically zero porosity, equal-grain structure, and elevated property indicators [20, 21]. In other words, there are ways to obtain materials with prescribed characteristics, right up to the maximum values, in practice characteristic of a particular oxide with its own crystalline structure.

The introduction of controllable impurities opens up even greater possibilities for regulating the structure of ceramics and thereby their properties. This is especially effective in chemical processes for obtaining powders, since they



provide the possibility of attaining a high purity and high degree of particle dispersity. It is very important that the additive, even small quantities, be distributed uniformly with formation of a solid solution. It should be noted especially that the structure can be regulated at the level of the unit cell structure, which radically changes the properties of a ceramic. Thus, the introduction of adequate amounts of heterovalent additives into zirconium dioxide stabilizes the high-temperature cubic phase in a wide temperature interval. In the process, the electric properties of the ceramic change from an insulator to ionic semiconductor.

Thus, there now exist different ways to activate powders during sintering. Since the driving force of the process is surface tension, they are all based on the use of powder as the initial material. On the other hand, a ceramic sinters by means of diffusion, and the diffusion mechanism is vacancy (interstitial) diffusion. It is known that the diffusion coefficient can be written as

$$D \sim nw,$$

where  $n$  and  $w$  are the concentration and mobility of the vacancies, respectively.

Diffusion is an activated process, and the powder body must have enough energy to overcome the barrier. This energy can be supplied from the outside in the course of sintering or accumulated in the powder particles in the form of a free surface as well as structural defect or imperfections [22]. The possibility of activation is established by the Clausius – Clapeyron equation of state for a mole of the substance. As the product  $pV$  or the temperature increases, the free energy of the body increases.

For thermal activation, i.e., as temperature increases, which is technically quite easy to accomplish, both components of the diffusion coefficient in the fluctuations processes increase, but the increase is small.

Solids can exist in a metastable state for a long time because of their very high inertness. The energy supplied to a body in fast irreversible processes during comminution (mechanical activation) as well as chemical or physical – chemical transformations (chemical activation) accumulates in it. Thermodynamically, this is an increase of the product  $pV$ . Physically, this is an increase of internal stresses and the volume accompanying the deformation of chemical bonds or the formation of ions with partially compensated bonds as a result of the extended surface as well as the appearance of defects in the volume and on the surface of the particles. This energy dissipates during mass transfer, but it is associated with a considerable increase of the concentration and mobility of vacancies.

Additives also increase the product  $pV$ , just as in the preceding case. The amount of the heterovalent additive determines the vacancy concentration, and the structure of the particles establishes their mobility, depending on the density of defects in the structure. However, the energy arising with bond deformation is not dissipated in this case during mass

transfer, but rather it remains in the material in the form of an elevated vacancy concentration. In the present case, the rate of mass transfer increases similarly to thermal activation.

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